Chemical Transformations

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Abstract

The Advanced Simulation and Computing (ASC) Program is providing a number of overviews ("white papers") on subjects of interest to the Department of Energy (DOE) Defense Laboratories (Lawrence Livermore, Los Alamos, and Sandia National Laboratories) as a part of the process. The design of safe and secure systems requires a detailed understanding of the consequences of organic material behavior in both normal and abnormal environments. A number of classes of organic materials are either present or can interact with the systems. Those materials include high explosives, propellants, foams, plastics, and hydrocarbon fuels. The DOE is interested in transformational improvements in predictive capabilities for a broad class of applications.

Introduction

In preparation for the Predictive Science Academic Alliances Program bidder's workshop, a series of "white papers" are being prepared. The topic of this white paper is chemical transformations. Other white papers will be provided on other topics of interest to NNSA and their Defense Program Laboratories. In many cases, the physics of interest spans multiple white papers. The capability to predict the properties of various organic materials is of interest to the Advanced Simulation and Computing (ASC) program to support computational assessments of the safety and reliability of systems containing organics materials subjected to normal and abnormal environments. Organic materials of interest include a broad class of energetic materials, potting foams, and various plastics. Relevant research topics include:

- calculation of decomposition rates under ambient and extreme conditions,
- condensed phase molecular interaction potentials,
- physical properties and transport coefficients,
- thermodynamic properties of organic materials,
- fuel combustion and soot formation, and
- aging effects in organic materials.

These elements have in common the need to develop experimentally verified computational methods that have a strong foundation in basic physical principles. They will generally have to be implemented to run efficiently on advanced parallel computing platforms to achieve sufficient accuracy. We describe each of these research areas in more detail in the following sections:

Calculation of Decomposition Rates

Energetic materials and other organic materials are metastable and will decompose at some rate under every condition. For energetic materials, chemical processes determine the detonation properties. The decomposition properties of organic and energetic materials, however, are controlled

by reaction kinetics. Furthermore, reaction history changes the properties of these materials, so we must model not just the "pristine" state, but also the properties that evolve as reactions occur.

The typical approach uses quantum calculations of intramolecular potential energy to determine the reaction pathways. Molecular dynamics approaches are then used to describe how the condensed system modifies the rates associated with these pathways. Such calculations are widely done now for gas phase reactions, with condensed phase simulations now becoming feasible. Determining the effect of the condensed state on the rates is the challenge, both in how this alters the fundamental reaction kinetics and in how partitioning of products and energy between the condensed and gas phase occurs. For some of the extreme temperature and pressure conditions accessible (e.g. detonation shocks), the effects of ionization, excited states and radiation transport might also be of significance.

There are several significant challenges associated with this area. First is the need to develop large-scale quantum chemistry programs so that reaction pathways under the appropriate conditions of pressure and temperature can be studied. As unanticipated reactions resulting from many-body interactions are highly likely, extrapolation from gas-phase or ambient conditions is not expected to be very predictive. Second, this knowledge of behavior needs to be captured accurately within a reactive molecular dynamics force field so that longer time and larger scale simulations can be performed. Third, these simulations typically rely on classical molecular dynamics that ignore significant quantum corrections to the vibrational partition functions. Thus, there are likely to be significant corrections to the temperature and partitioning of the kinetic energy. Fourth, the resulting dominant reaction paths need to be distilled into effective chemistry models that can be utilized within continuum / mesoscale simulations. This will likely involve disparate time scales of the rapid generations of distinct molecular products (nitrogen, water) and more extended reaction-diffusion processes of carbon clustering reactions (soot) and metal oxide formation. Finally, those implemented models need to be verified for both accurate integration of the kinetics, and for partitioning of products and energy between the phases in the simulation.

Another challenge is that many of the reactions of interest occur in heterogeneous solid composites. Fundamental progress must be made on the reaction kinetics of solids, where chemical processes are often mediated by defects. The slow decomposition of organic solids often leaves behind ill-characterized materials that are difficult to describe with traditional chemical kinetic schemes.

High explosives create extreme pressures (up to 500 kbar) and temperatures (3500 K) during the detonation process. These extreme conditions push the boundaries of molecular matter. For instance, water has been found to undergo a molecular to superionic transition at 450 kbar and 1300K. At pressures above 450 kbar, water is no longer a molecular material. A unified theory of the transition from molecular to non-molecular matter does not exist. The boundaries of molecular matter need to be established through first principles simulations and experiment. This class of transformations is challenging to model with conventional molecular interaction potentials.

Molecular Potential Functions

Molecular potential functions form the foundation for predicting the properties of organic composite material systems. Simple (or fairly simple), transferable potential-energy functions for explosive,

energetic, and inert organic molecules, parameterized over a wide range of conditions, are fundamental to modeling activities for weapons performance, safety, reliability, and renewal/manufacturing. Prediction of the performance and safety of organic materials necessitates interaction potentials accurate over a wide range of pressures. Modeling the response of organic materials to a fire following a crash or to less severe long-term heating requires models applicable over the full range of accident scenarios that may lead to decomposition (and ignition in energetic materials). Predicting the impact of age on the performance and safety of organic materials not only requires molecular interaction potentials accurate at high temperatures and widely varying pressures but also over the wide range of environments experience by a weapon during its lifetime e.g. temperatures ranging from -120 ºF to 120 ºF). Finally, modeling manufacturing processes, as well as deriving new, improved materials requires a fundamental understanding of the structure-property relationships (nearly synonymous with accurate interaction potentials) of these materials under processing conditions as well as the performance and safety environments.

There are several motivations for this technology. The performance of energetic materials (propellants or explosives) is heavily reliant on their density, both in terms of the energy and number of product molecules that are effectively present in the initial structure. Transformations to alternative structures by some physical inducement are likely having deleterious effects, though it might be possible to engineer beneficial aspects into this. Physical properties will depend on the molecular packing, both thermally (expansion coefficients and phase transitions) and mechanically (accessible slip planes). The behaviors of polymeric materials are heavily tied to aspects such as the volume and distribution of crystalline regimes, the free volume in amorphous regions (for flexibility and molecular diffusion processes), and phase separation and surface adhesion properties.

Potential-energy surfaces for "generic" crystals have been developed for hydrocarbons and azabenzenes, though these reveal challenges in accurate anticipation of packing motifs and thermal corrections Potential energy surfaces for the most important molecules in high explosives and energetic materials, such as the nitramines and nitrated/aminated benzenes, present an even greater challenge because of access to multiple molecular conformations, and significant thermal motions in low energy torsional and conformation modes. Electrostatic interactions for these more polar species are critical for an accurate description of their packing, where static monopolar atomic charges are likely insufficient to capture the subtleties of the steric and electrostatic effects due to the presence of lone pair electrons, and changes in charge distribution due to conformational changes. In addition, the calibrations for these potential functions should be extended beyond ambient conditions to much higher temperatures and pressures to be relevant to explosive reaction zones. As for the reaction kinetics, corrections for zero-point energies and effective thermal motions need to be included.

Thermophysical Properties and Transport Coefficients

Physical properties and transport coefficients from the molecular scale to larger distance and time scales are needed to advance the simulation of organic materials. Starting from molecular potential functions it should be possible to provide, from first principles, many of the required fundamental physical parameters. The physical properties that must be calculated include density, energy, specific heat, vector and scalar coefficients of thermal and isobaric expansion, elastic constants and derived moduli, mechanical strength, all as a function of temperature and pressure for both solids and

liquids. There has been recent significant development of practical methods to compute stress-strain curves and transport coefficients such as diffusion, viscosity, and thermal conductivity, though there is a need to extend these to non-linear regimes. These are harder to obtain due to the more complicated theoretical framework required.

The response to abnormal thermal and mechanical stimuli is also determined by porosity, permeability and tortuosity of the material. Most work has been applied to either perfect crystals or a random, isotropic fluid state. Corrections for non-ideal aspects need to be considered, as well as accurate extensions to polymeric materials where low levels of structure will be present. The thermodynamic properties of polymeric foams and other organic materials under conditions of extreme temperature and shock are important to ASC. Continuum-scale response models based on fundamental physical and chemical properties are needed as well as an improved understanding of these phenomena at the atomic scale.

A variety of theoretical tools are required to do these calculations. They include high-level *ab initio* quantum electronic structure methods, Monte Carlo methods, and both classical and quantum mechanical molecular dynamics. The full spectrum of modern computing capabilities must be brought to bear in this work, from high-performance workstations in stand-alone mode and in clusters, to advanced high-end parallel platforms. Coupling of electronic structure methods and classical simulations would be advantageous in assessing the behavior of non-ideal structures (ie ideal crystal or isotropic fluid).

Mechanical Properties of Organic Materials

The mechanical properties of organic crystals, melts and polymeric materials, especially under conditions of elevated temperature and pressure, are important to ASC. Specific technical areas of interest include:

- Ab initio electronic structure calculations of point defects and dislocations to determine energetic and fundamental length scales
- Atomic-level simulations of dislocations and dislocation interactions to derive rules and mechanisms for microstructure-level simulation
- Three-dimensional (3D) dynamic dislocation simulation of microstructure and plasticity and mesoscale studies of polycrystalline grains to develop improved plasticity models
- The connection to mesoscale and continuum-based models of improved anisotropic plasticity models.

Most of the relevant mechanical aspects are described in the white paper relating to constitutive properties. What is of greater relevance here is how this affects the chemical reaction properties? One example is the generation of excess temperature (and its persistence) associated with dislocation dynamics or other localized stress features (eg void collapse) and how that may influence the effective chemical dynamics models. The possibility of anisotropic mechanical induction of a reaction (e.g., mechanical rather than thermal induced scission of bonds) should also be considered, where this is certainly a factor in the failure of polymeric materials. Conversely, reaction within a localized deformation zone should effectively lubricate it by the generation of small molecules and disruption of the local structure, and enhance further localization of the displacement in that region.

Consequently, chemical reaction will become a substantial perturbation to mechanical property predictions in certain regimes.

Fuel Combustion and Soot Formation

Accident scenarios (also known as abnormal environments) generally involve the combustion of organic materials such as jet and diesel fuel. Fine soot particles are also formed during the detonation of a high explosive. Thermal insult due to pool fires is an abnormal environment scenario required for the qualification of weapons systems. The primary mechanism for energy transfer to a system is radiation from the soot produced in a fire. Fires involve highly non-linear phenomena including fluid transport, combustion, and radiation. The nonlinear "turbulence problem" common to all high Reynolds number flows is amplified in fires in that turbulence affects convective stirring down to millimeter length scales at which flame zones reside. The non-linear mixing rates control combustion; and therefore, heat release rates and temperatures. Further, radiation heat transfer is dependent on the soot temperature to the fourth power while soot absorption coefficients result in exponential decay of thermal radiation spatially.

Fires involve phenomena that are tightly coupled. Fire is the natural balance between all physical phenomena. This coupling is tighter than most combustion phenomena where some external control exists on either the momentum or scalar flow fields (i.e., the inlet velocities, or fuel/air ratios). Fire is not a process with inputs and outputs in the usual sense, rather a balance point that is a result of the circular closure of the mechanisms. As an example, heat flux to a liquid pool surface results in fuel vaporization. The vaporized fuel mixes with air and ignites which results in flames. Radiative heat transfer from the flames results in a heat flux to the liquid pool surface which results in fuel vapor, and the process repeats itself. If any change occurs in any of the flow conditions, i.e., geometry, wind, fuel, etc. the balance point will shift to a new equilibrium point. The fire will then be a different fire with different combustion rates, temperatures, and radiative heat fluxes. In the same vein, the vortical structures which are found at all length scales in a fire can simultaneously be interpreted as being the consequence of the heat release in a fire and as the cause of the heat release in a fire.

Soot formation during detonation is not well understood, yet is the key to understanding the release of energy during the detonation process. Many insensitive explosives are carbon-rich. A significant fraction of the energy release of these materials comes from the formation of carbon particles. Detonating explosives have been found to produce nano-diamond and other exotic carbon morphologies. The processes and time scales controlling the formation of carbon clusters under extreme conditions, however, remains poorly understood. A particular challenge is that the carbon cluster formation timescale is believed to require up to a microsecond, making the direct application of molecular dynamics methodologies difficult.

Chemical Aging Effects in Organic Materials

Results in the other research elements may be dramatically affected by the aging process. By their very nature, organic materials are metastable molecules. Therefore, over time, they will decompose, produce gas, and at higher temperatures change molecular composition and structure. These changes

lead to changes in the macroscopic behavior of these materials and can have profound nonlinear effects on systems containing them.

Degradation mechanisms and chemical reactions must be addressed to understand the performance consequences of aging in organic materials. The effects of aging on transport coefficients are important for other issues as well, such as the outgassing of binders and plasticizers in aging energetic materials. Polymeric materials undergo physical aging processes, as well as chemical, where this includes continual refinement in structure (phase separation, crystallization) as well as relaxation to accommodate local stress fields that may evolve with time. Crystalline materials may undergo similar physical ripening processes that might impact their subsequent effective chemical kinetics. The relationship of the composition of aged energetic materials to their initiation and detonation performance, mechanical response and response to abnormal thermal and mechanical stimuli must be addressed.

Aging processes related to organic materials including stress-voiding of integrated circuit interconnects, thermomechanical fatigue of solder joints, corrosion processes, oxidation and cross-linking in polymers, and plasticizer outgassing and reactive degradation of energetic materials are poorly understood. Mobile products from the degradation of organic materials can contribute to the corrosion of neighboring metallic components, enhancing crack growth or similar phenomena. Much work is needed to understand the physical and chemical processes underlying predictive failure models for these aging processes. Models and experimental validation are needed for phenomena such as void nucleation and growth, impurity migration, microstructural evolution in metals, fracture precipitation and propagation mechanisms, reactive degradation chemistry, and diffusion in high molecular weight materials. Accelerated aging experiments and methods development are also needed for model validation.

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